

Electron Microscope Visualization of Multiphase Fluids Contained in Closed Carbon Nanotubes

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Abstract : Aqueous multiphase fluids trapped in closed multiwall carbon nanotubes are visualized with high resolution using transmission electron microscopy (TEM). The hydrothermally synthesized nanotubes have inner diameter of 70 nm and wall thickness 20 nm, on average. The nanotubes are hydrophilic due to oxygen groups attached on their wall surfaces. Segregated liquid inclusions contained in the nanotubes under high pressure can be mobilized by heating. A resistive heating stage is utilized to heat a thin membrane inside a nanotube, causing the membrane to evaporate slowly and eventually pinch off. Focused electron beam heating is employed as a second means of thermal stimulation, which results in localized heating. With the latter method, gas/liquid interface motion is observed inside the thin channel of a carbon nanotube. Experiments like the ones presented herein may help understand the dynamics of fluids contained in nanoscale channels.

Keywords : Multiphase fluid, Carbon nanotubes, Electron microscopy, Interface.

1. Introduction

Carbon nanotubes (CNTs) have attracted immense scientific interest since they were discovered in 1991 (Iijima, 1991). Since then, most research studies in this area have focused on nanotube structure as well as mechanical, electronic, and transport properties (Saito et al., 1998). Nanotubes are very strong and flexible; for example, Young's modulus for multiwall carbon nanotubes has been shown to be approximately 1 TPa; it has been predicted that this quantity would be similar for single-wall carbon nanotubes (Baughman et al., 2002). Carbon nanotubes can be metallic or semi-conducting, depending on their diameter and chirality (Dresselhaus et al., 1996). Carbon nanotubes also possess extremely high thermal conductivity k along the axial direction; Kim et al. (2001) reported experimental values of k as high as 3000 W/m K.

Since straight, multiwall, hollow CNTs can potentially be utilized as conduits in microfluidic devices, it is important to investigate fluid behavior in these nanochannels (Koumoutsakos et al, 2004), which provide an excellent opportunity to identify how multiphase fluids respond to external stimuli at the nanoscale. A powerful tool to visualize fluid behavior in closed thin-walled channels is the transmission electron microscope (TEM). Not only does this instrument allow visual detection of

liquid volumes trapped inside CNT channels, but also focusing and expanding of the electron beam can be used as a means of heating or cooling such liquids, thereby creating fascinating fluid dynamic phenomena (Gogotsi et al., 2001a; Megaridis et al., 2002). Moreover, a heating stage may be utilized within the TEM to increase/decrease the temperature of the specimen in a controlled manner. In this paper, observations of fluid dynamic phenomena in response to both means of thermal stimulation inside closed, multiwall CNTs are presented.

2. Experimental Procedures

2.1 Nanotube Synthesis and TEM Specimen Preparation

The multiwall carbon nanotubes utilized in this work were produced hydrothermally at the University of Illinois at Chicago. De-ionized water, ethylene glycol (carbon source), and nickel (catalyst) were first sealed into gold capsules; the mixture was then reacted at high pressure (up to 80 MPa) and temperature (770°C) for 21 hours; see Libera and Gogotsi (2001). Hydrothermal synthesis allows the entrapment of the supercritical liquid inside the CNTs during synthesis. As the products in the sealed capsule are brought down to room temperature and pressure, the sealed CNTs retain the aqueous multicomponent fluid under high pressure without leakage. The fluid components, as predicted by thermodynamic calculations performed at synthesis conditions (Gogotsi et al., 1998), are 85.2% H₂O, 7.4% CO₂, 7.4% CH₄, with traces of H₂ and CO (Gogotsi et al., 2002). Although the CNT fluid contents may be contained at supercritical pressures (up to 30 MPa, see Gogotsi et al., 2001b), the temperature is well below the critical value, thus resulting in the presence of clearly defined interfaces distinguishing gas from liquid volumes. After removal from the capsule, the run products are dispersed in ethanol, sonicated, and the nanotube-containing liquid is deposited onto lacey carbon film coated copper TEM grids for further analysis. The nanotubes remain attached to the film after evaporation of the liquid carrier.

2.2 TEM Analysis

The TEM used in this study is a JEOL JEM-3010, 300 keV with 0.14nm lattice resolution. It is equipped with a digital camera, which allows still images to be collected on a Gatan digital imaging system with a computer running Digital Micrograph software. Moreover, a BetaCam video recorder was attached to the microscope for video recording of dynamic fluid phenomena.

The TEM was used for imaging isolated nanotubes at the midplane [see Fig. 1(a)], where the lattice image has maximum contrast. The latter is a result of the fact that the electron beam encounters the most carbon atoms at the midplane, where these atoms remain organized in graphite-like walls parallel to the beam. The interface curvature is also parallel to the beam at the midplane. Figure 1(b) presents how the electron beam is focused on this plane to create the image of a fluid-filled CNT. The electrons of the concentrated (focused) TEM beam were employed as a heating source, inducing fluid motion inside isolated CNTs, as shown in Gogotsi et al. (2001a) and Megaridis et al. (2002). The gas/liquid interfaces of the aqueous multiphase fluid were used as markers of liquid volume motion. Alternative to focused electron beam heating, a resistive heating stage was also used to thermally excite the nanotubes. While a contracted electron beam is a convenient means of achieving rapid or gentle heating of the illuminated area, it may impose substantial temperature gradients from the illuminated to the remote portions of the CNT and lead to radiolysis of water or beam-induced damage of tube walls. On the other hand, the heating stage, which employs a resistive heater, allows to gradually raise the temperature of the entire grid, thus eliminating any appreciable local temperature gradients. It also allows experiments at a given high or cryogenic temperature and experiments with a constant heating rate, which are impossible when using just the electron beam. The exact temperature of the sample when electron beam heating was used in our previous TEM studies (Gogotsi et al., 2001) is not known. Examples of both of these methods of thermal manipulation of fluid-filled CNTs are presented below.

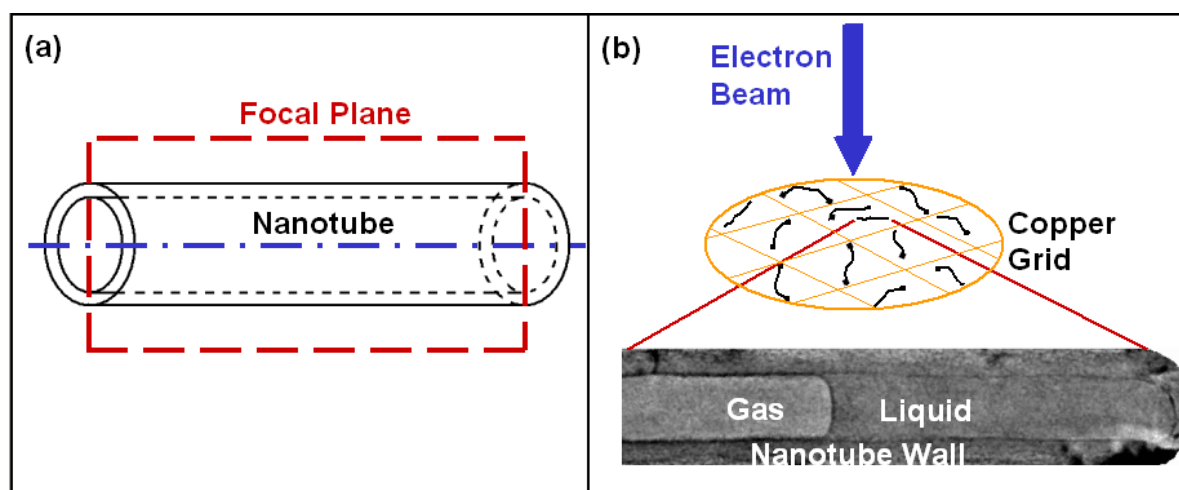


Fig. 1. (a) Optimal focal plane for nanotube imaging in a TEM. (b) When the electron beam is focused on a CNT resting on a grid, the CNT fluid contents and their interfaces come into view.

When the concentrated electron beam is used as a means of heating a nanotube, the absorption of energy is dependent on a few factors. The most important factor is the amount of material, i.e., material density. For example, solid materials will absorb more energy than liquids. However, energy absorption also depends on the degree of beam focus. Another factor is atomic number; higher atomic number elements absorb more. Lastly, material thickness also plays an important role. A thick-walled CNT will absorb more energy than a thin-walled CNT. All of these factors interplay with each other and other parameters such as alignment, focusing, and beam intensity to result in a complex heating arrangement.

If the microscope is well aligned and the beam is focused, the electrons converge at the center of a CNT and result in volumetric heating of the fluidic contents, even though the absorption may be quite low. In principle, absorption is a result of inelastic scattering (less than 10% of incident electrons). On rare occasions, inelastic scattering may lead to sample damage by knocking atoms out of the lattice. During conventional TEM imaging, elastic scattering of the electrons and diffraction occur, thus allowing the formation of an image on the observation screen (Fig. 2).

3. TEM Observation of Fluid Motion and Phase Transitions

Figure 3 is a sequence of TEM images extracted from the digital video record of an experiment, where an aqueous volume bordered by two gas bubbles was subjected to heating at a rate of $40^{\circ}\text{C}/\text{min}$ using the heating stage. In the early stages of heating, the liquid volume contracted as the temperature of the stage increased. With continuously increasing temperature, the membrane pinched off when the stage temperature read $\sim 260^{\circ}\text{C}$, 6 minutes after the onset of heating at this rate. The liquid eventually disappeared from the field of view. This pinch-off event was irreversible; the liquid membrane could not be re-created after cooling down. Since local temperature gradients cannot be sustained with the heating stage, thermocapillarity may be excluded as an important fluid transport mechanism affecting the volume change in Fig. 3. It appears that temperature-dependent diffusion and phase change drive the observed fluid transport dynamics.

Figure 4 displays an interesting mode of gas/liquid interface propagation with time in response to electron beam heating. The initial state of the gas/liquid interface is similar to the one seen in Fig. 3. With an increase in temperature, a complex interface forms between the gas and the liquid, as shown in Fig. 4(a). As heating is sustained, this interface moves from left to right, in the form of repeated bubble formation in the adjoining liquid [Figs. 4(b-d)]. As two neighboring bubbles expand, the liquid in between pinches-off near the tube axis, similar to the pinch-off seen in Fig. 3, thus forming the wave-like pattern on the inner tube wall [Figs. 4(d-e)]. However, compared to Fig. 3, the

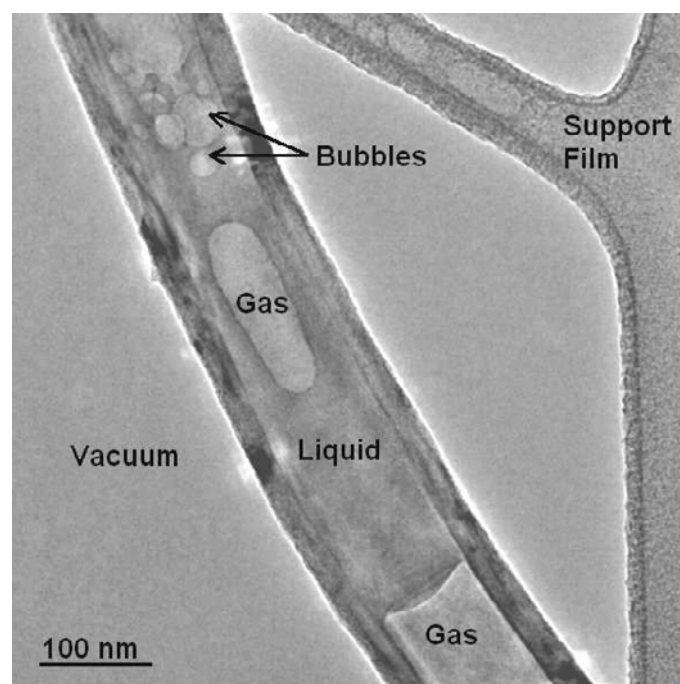


Fig. 2. TEM image from a dynamic heating experiment on a fluid-filled CNT. The nanotube, which is heated by the focused electron beam, contains liquid, gas, as well as bubbles at this instant. The lower gas/liquid interface appears to have a complex shape, as compared to the interface shown in Fig. 1(b).

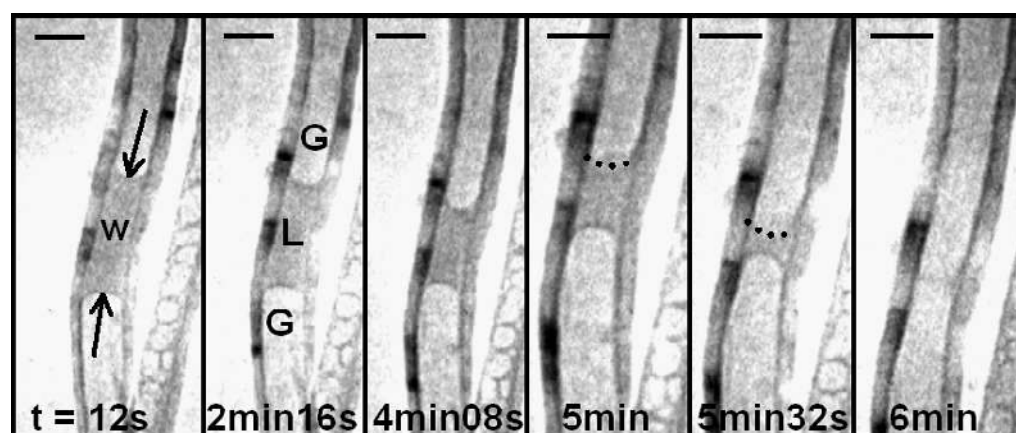


Fig. 3. TEM temporal sequence of an aqueous liquid volume encapsulated inside a CNT, and subjected to heating with the resistive stage. The liquid slowly evaporates and pinches-off after ~6 min. In frames 4 and 5, the top interface is marked with a black dotted line. Scale bar corresponds to 100nm.

liquid in Fig. 4 appears to be less mobile, thus taking more time to spread smoothly along the nanotube wall after pinch-off. The film thickness on the inner wall is up to 10nm initially, and decreases with prolonged electron beam heating [Figs. 4(d-f)], as the gas/liquid interface also smooths out.

The amount of energy delivered as heat by the electron beam to a fluid-filled CNT is estimated in the following. The incoming electrons have energy of 300 keV, and as a result of interactions with the thin CNT specimen, fewer than 10% of the incident electrons lose on average 20 eV (Marton, 1965). The energy loss is due to inelastic scattering in the specimen, and depends on the structure of the CNT as well as its fluid content. The measured specimen beam current is 200 pA. The illumination on a single CNT is estimated to be ~1% of this value, since one CNT occupies only a fraction of the visualized area. Taking into consideration the charge of an electron and the electron

bombardment frequency, the total electron energy loss (i.e., energy absorbed by the specimen) is estimated to be $\sim 5 \times 10^{-12} \text{W}$. Assuming a heated fluid volume of $\sim 10^2 \times 10^2 \times 10^2 = 10^6 \text{nm}^3$, the heating power input density is estimated to be $5 \times 10^6 \text{kW/m}^3$. This power input is typical of that produced in a nuclear power plant.

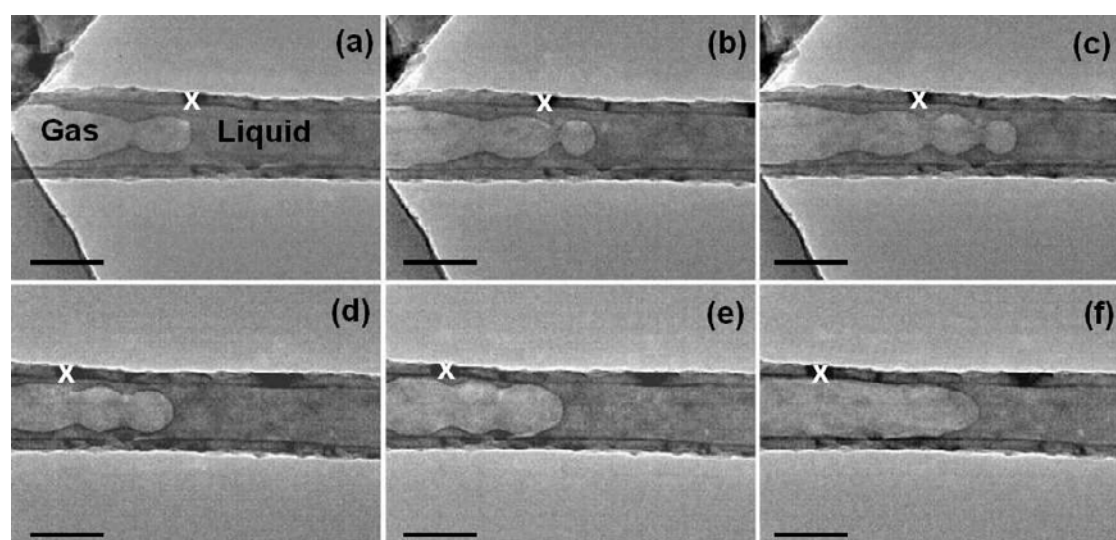


Fig. 4. Time sequence of TEM images displaying gas/liquid interface propagation upon sustained constant heating with electron irradiation. A complex interface forms in (a), then moves from left to right via repeated bubble formation in the adjoining bulk liquid. The white x on the top marks a fixed location on the CNT wall for better visualization of the relative interface motion. Parts of the supporting carbon film can be seen on the left side of frames (a-c). Scale bar denotes 70nm.

A fascinating observation, which was recorded during a resistive heating stage experiment, is presented in Fig. 5. Initially, the CNT shown contained a long liquid inclusion adjacent to a vapor bubble. This liquid was heated via the resistive stage to a temperature of 300°C at a rate of $25^\circ\text{C}/\text{min}$, during which it evaporated slowly, as revealed by the smooth retraction of the interface towards the lower left side of the nanotube (not shown). When the target temperature (300°C) was reached, heating was ceased and the resistive stage temperature was set to 30°C . As cooling proceeded by heat losses, rapid condensation of the vapor occurred at 178°C , as indicated by a sudden liquid/vapor interface “jump” from Fig. 5(a) to Fig. 5(b). This jump occurred in less than $1/10$ of a second. Similar slow evaporation and very fast condensation of water in carbon nanotubes was also observed in environmental SEM experiments conducted at low pressure and 4°C (Rossi et al, 2004). Further cooling resulted in another “jump” of the interface about one second later with the same rate, from Fig. 5(c) to Fig. 5(d). When room temperature was reached, a second heating/cooling cycle was started and the whole sequence could be repeated. The liquid first evaporated during heating to 300°C , then condensed during cooling-down to room temperature. At about 180°C , the sudden jump was observed again. In these sequences rapid condensation occurs at elevated temperatures, which, in turn, suggests elevated containment pressures (saturation pressure of water at 180°C is about 1 MPa), thus confirming our earlier evaluation (Gogotsi et al., 2001b) that the fluid is contained at high pressures. However, it is necessary to note that no convection or radiation heat transport occurs in the high vacuum of the TEM chamber at the temperatures applicable to Fig. 5. Since nanotubes have only limited contact with the holey carbon film, which possesses a low thermal conductivity, it is plausible that the temperature of the nanotube contents may be somewhat different than the monitored temperature of the copper grid.

The phenomenon seen in Fig. 5 seems similar to the well-known “water hammer” effect occurring in hot water pipe systems. If the vapor shown in Fig. 5 rapidly gave up its energy to the

adjacent liquid or the nanotube walls, it could rapidly assume a liquid state, thus decreasing its volume by a large factor, depending on the saturated vapor pressure. The pressure in the “void” caused by the sudden condensation of the vapor is reduced to the saturated vapor pressure of the nearby liquid, thus attracting the liquid to rush towards it, thereby creating the “jumps.” Although this explanation is plausible, it is not clear why such a phenomenon occurred in the CNT of Fig. 5 and not in other fluid-filled CNTs that were subjected to similar stimuli.

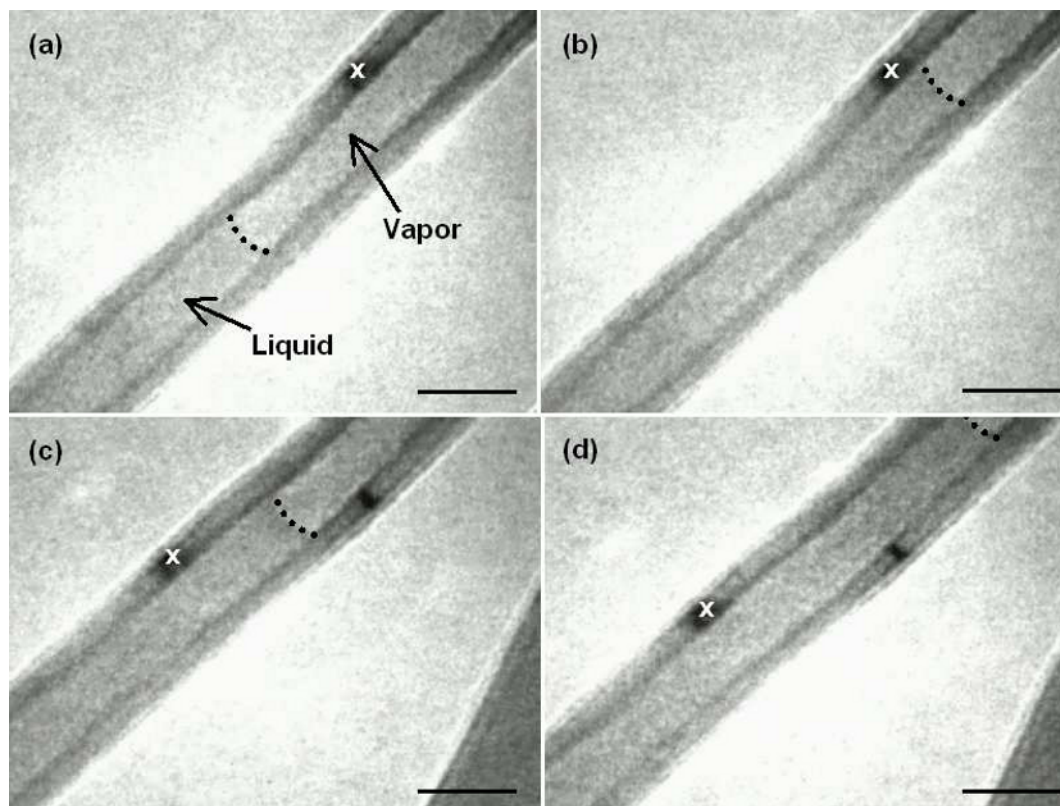


Fig. 5. TEM images of a rapid cooling sequence of a liquid inclusion constrained by vapor on one side and an end cap on the other (not shown). The gas/liquid interface is traced with the black dotted line. The white x on the nanotube wall marks a fixed location for better visualization of the relative interface location. The interface “jumps” twice [(a) to (b) and (c) to (d)] due to rapid condensation. Scale bar denotes 100nm.

While liquid water can only be studied inside closed tubes in TEM, solid water (ice) can be investigated on the outer surface of nanotubes as well. A cold microscope stage uses liquid nitrogen to cool TEM specimens using a copper rod for conduction. Such a cold stage was employed in one experiment to observe water-filled small CNTs under extreme temperature conditions inside the electron microscope. At steady state, the temperature of the stage, therefore the nanotube-containing copper grid, was -178°C . Figure 6 illustrates an ice sublimation sequence observed when a small bundle of carbon nanotubes was subjected to electron beam irradiation. The ice had formed as a result of freezing water when brought into the TEM column along with the CNT sample dispersed on the grid. The volume of the ice block shown in Fig. 6(b) was calculated as approximately $4.8 \times 10^{-21} \text{m}^3$, assuming cylindrical geometry. Taking into consideration the latent heat of sublimation of ice, $2.8 \times 10^6 \text{J/kg}$ (Cengel, 2002), and the density of water, $\sim 1000 \text{kg/m}^3$, the energy input to the ice-covered CNTs by the electron beam for complete sublimation, which lasted 25 seconds in this case, must be $\sim 5 \times 10^{-13} \text{W}$. This value is by one order of magnitude lower than the beam energy input of $5 \times 10^{-12} \text{W}$, estimated earlier using inelastic scattering considerations. Some of the energy provided by the electrons in Fig. 6 could be conducted away from the illuminated region by the nanotubes and not used in the sublimation process, thus explaining the difference.

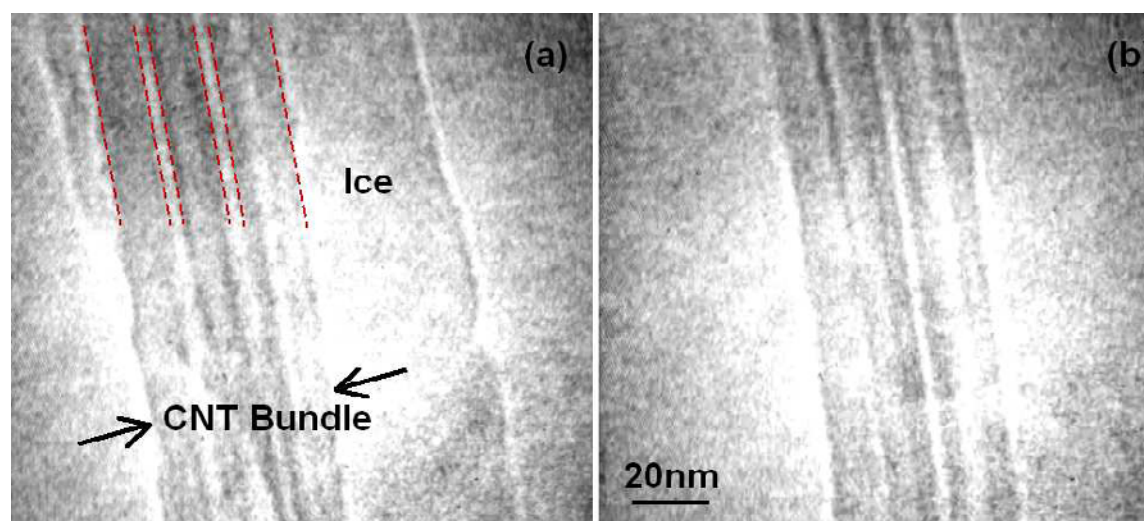


Fig. 6. Two still snapshots from a video recording of sublimating ice covering a small bundle of carbon nanotubes. (a) The ice covers the nanotubes initially. Red lines indicate individual nanotubes. (b) After 25 seconds of illumination with the electron beam, the ice sublimates entirely.

4. Conclusion

Multiwalled closed-end carbon nanotubes encapsulating a high-pressure multiphase aqueous fluid have been utilized in nanoscale fluidic experiments where fluid motion and phase change were monitored in real time using a transmission electron microscope. These nanotubes are thin enough to be nearly transparent to the electron beam, while being thick and strong enough to contain fluids at high pressure in the high vacuum atmosphere of the electron microscope. The results presented in this work demonstrate that transmission electron microscopy is a powerful technique for visualizing multiphase fluids trapped in nanochannels.

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References

- Baughman, R. H., Zakhidov, A. A. and de Heer, W. A., Carbon nanotubes-the route towards applications, *Science*, 297 (2002), 787-792.
- Cengel, Y. A., *Thermodynamics: An Engineering Approach* (4th ed.), (2002), McGraw-Hill, New York.
- Dresselhaus, M. S., Dresselhaus, G. and Eklund, P. C., *Science of Fullerenes and Carbon Nanotubes*, (1996), Academic Press, San Diego.
- Gogotsi, Y., Kraft, T., Nickel, K. G. and Zvanut, M. E., Hydrothermal behavior of diamond, *Diam. Rel. Mat.*, 7 (1998), 1459-1465.
- Gogotsi, Y., Libera, J., Yazicioglu, A. G. and Megaridis, C. M., In situ multiphase fluid experiments in hydrothermal carbon nanotubes, *App. Phys. Lett.*, 79 (2001a), 1021-1023.
- Gogotsi, Y., Libera, J., Yazicioglu, A. G. and Megaridis, C. M., In situ fluid experiments in carbon nanotubes, *MRS Symposium Proc. (Boston)*, 633 (2001b), A.7.4.1-A.7.4.6.
- Gogotsi, Y., Naguib, N., Ye, H., Yazicioglu, A. G. and Megaridis, C. M., Analysis of fluid in hydrothermal carbon nanotubes, *Proc. Electrochemical Soc. (Philadelphia)*, 12 (2002), 451-459.
- Iijima, S., Helical microtubules of graphitic carbon, *Nature*, 354 (1991), 56-58.
- Kim, P., Shi, L., Majumdar, A. and McEuen, P. L., Thermal transport measurements of individual multiwalled nanotubes, *Phys. Rev. Lett.*, 87 (2001), 215502-1-4.
- Koumoutsakos, P., Zimmerli, U., Werder, T. and Walther, J. H., *Nanoscale Fluid Mechanics*, ASME/SPIE Handbook of Nanotechnology: Nanometer Structure: Theory, Modeling, and Simulation, (2004), 319-393.
- Libera, J. and Gogotsi, Y., Hydrothermal synthesis of graphite tubules using Ni catalyst, *Carbon*, 39 (2001), 1307-1318.
- Marton, L. L., Experiments in electron scattering. II, *Laboratory Investigation*, 14 (1965), 745-761.
- Megaridis, C. M., Yazicioglu, A. G., Libera, J. A. and Gogotsi, Y., Attoliter fluid experiments in individual closed-end carbon nanotubes: Liquid film and fluid interface dynamics, *Phys. Fluids*, 14 (2002), L5-L8.
- Rossi, M. P., Ye, H., Gogotsi, Y., Babu, S., Ndungu, P. and Bradley, J.-C., Environmental scanning electron microscopy study of

water in carbon nanopipes, *Nano Letters*, 4 (2004), 989-993.
 Saito, R., Dresselhaus, M. S. and Dresselhaus, G., *Physical Properties of Carbon*, (1998), Imperial College Press, London.

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